

epoxy group, an oxetane group, an acryl-epoxy oligomer group or a methacryl-epoxy oligomer group, or at least one resin composition comprising at least one polymerisable polysiloxane,

- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator, and
- (d) 0-85 wt.% of one or more modifiers selected from the group consisting of fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

<sup>27</sup>  
<sup>24</sup>. The method according to claim <sup>26</sup>~~23~~, further comprising producing models, individually manufactured single products or mass-produced sales products.

<sup>28</sup>  
<sup>25</sup>. The method according to claim <sup>26</sup>~~28~~, wherein constituent (a) comprises an ormocer.

<sup>29</sup>  
<sup>26</sup>. The method according to claim <sup>26</sup>~~23~~, wherein constituent (a) is a resin composition comprising polymerisable polysiloxanes, which can be hardened photochemically or thermally, in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon, wherein 1 to 100 mole %, based on the monomeric compounds, are selected from

- (i) silanes of the general formula (I),



wherein the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl, or NR'<sub>2</sub>

where R' = hydrogen, alkyl or aryl,

Y = a substituent, which comprises a substituted or unsubstituted 1,4,6-trioxaspiro-[4,4]-nonane radical,

n=1, 2 or 3,

m=1, 2 or 3,

where n+m ≤ 4,

and/or from

(ii) silanes of the general formula (II),



wherein the radicals A, R, R<sup>2</sup> and X are the same or different, where all variables have the same meaning as defined above, and

A = O, S, PR', POR', NHC(O)O or NHC(O)NR',

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for l = 1 and A = NHC(O)O or NHC(O)NR') or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R<sup>2</sup> = alkylene, arylene or alkylene-arylene,

k = 0, 1 or 2,

l = 0 or 1, and

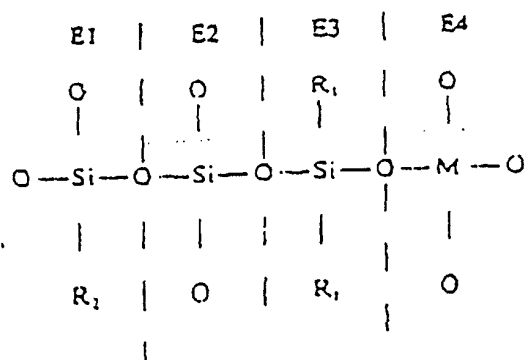
x = a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B', when l = 1 and A represents NHC(O) or NHC(O)NR'.

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A'  
cont

<sup>30</sup>  
27. The method according to claim <sup>2</sup>30, wherein the polymerisable polysiloxane further comprises a hydrolytically condensable compound of an element selected from the group consisting of B, Ba, Ti, Zr, Al, Sn, the transition metals, the lanthanides and the actinides, or a pre-condensate derived from the above-mentioned compounds.

<sup>31</sup>  
28. the method according to claim <sup>26</sup>23, wherein constituent (a) is a resin composition comprising a compound composed of the structural element E 2 and at least one of the structural elements E 1, E 3 or E 4 of the general formula



wherein:

R<sub>1</sub> denotes a methyl, ethyl, n-propyl, isopropyl or an optionally CH<sub>3</sub>-C<sub>3</sub>H<sub>7</sub>-substituted phenyl radical,

R<sub>2</sub> denotes a CH<sub>2</sub>=CH, CH<sub>2</sub>=CHCOO(CH<sub>2</sub>)<sub>n</sub> or CH=C(CH<sub>3</sub>)-COO(CH<sub>2</sub>)<sub>n</sub> radical, or R<sub>1</sub>,

n denotes 0, 1, 2 or 3, and

M denotes titanium or zirconium.

<sup>32</sup>  
29. The method according to claim <sup>26</sup>23, wherein constituent (a) is present in a quantity of 10-95 wt. %.

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<sup>33</sup>  
~~30~~. The method according to claim <sup>26</sup>~~28~~, further comprising hardening the composition using a wavelength range from 350-700 nm.

<sup>34</sup>  
~~31~~. The method according to claim <sup>26</sup>~~23~~, wherein constituent (a) comprises a component selected from the group consisting of aliphatic diurethane methacrylate, tetraethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates, 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate, 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 1,3,5,7,9-pentakis-3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexy-15,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane, bis-(3,4-epoxycyclohexylmethyl) adipate, monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl

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ether, triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether, ethylene glycol-monovinyl ether, diethylene glycol divinyl ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether and 2-diethylaminoethyl-vinyl ether.

<sup>35</sup>  
~~32~~. The method according to claim <sup>26</sup>~~23~~, wherein constituent (b) comprises:

for free-radical hardening, a component selected from the group consisting of phosphine oxides, benzoin ethers, benzil ketals, acetophenones, benzophenones, thioxanthenes,  $\alpha$ -dicarbonyl compounds, bisimidazoles, metallocenes, aryl-tert.-butyl peresters and fluorones, or

for cationic hardening, a component selected from the group consisting of aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and phenylphosphonium-benzophenone salts,

or a mixture thereof.

<sup>36</sup>  
<sup>35</sup>  
33. The method according to claim <sup>35</sup>~~32~~, wherein constituent (b) comprises a component selected from the group consisting of diphenyl-2,4,6-trimethylbenzoylphosphine oxide, benzoin, benzoin-alkyl ether, benzildialkyl ketals,  $\alpha$ -hydroxyacetophenone, dialkoxyacetophenone,  $\alpha$ -aminoacetophenone, i-propylthioxanthone, camphor-quinone, titanocene, ferrocene, and 5,7-diiodo-3-butoxy-6-fluorone.

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<sup>37</sup>  
34. The method according to claim <sup>26</sup>~~23~~, wherein constituent (c) comprises:

for free-radical hardening, a component is selected from the group consisting of tertiary amines, diaryl iodonium compounds, borates, organic phosphites and thioxanthenes,

for cationic hardening, a component is selected from the group consisting of xanthenes, fluorenes, fluorones and/or  $\alpha$ -dicarbonyl compound, or a mixture thereof.

<sup>38</sup>  
35. The method according to claim <sup>37</sup>~~34~~, wherein constituent (c) comprises a component selected from the group consisting of N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine, and N,N-dialkyl-alkylaniline, butyrylcholine-triphenylbutyl borate.

<sup>39</sup>  
36. The method according to claim <sup>26</sup>~~23~~, wherein constituent (d) comprises an anthraquinone dyestuff.

<sup>40</sup>  
37. The method according to claim <sup>26</sup>~~23~~, wherein constituent (d) comprises a filler selected from the group consisting of silicon dioxide, pyrogenic silicon dioxide, amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glass, fragment polymer, silica gel, minerals, fibres and fabrics.

<sup>41</sup>  
38. The method according to claim <sup>40</sup>~~37~~, wherein constituent (d) comprises a fibre selected from the group consisting of glass fibres, carbon fibres, textile fibres and metal fibres, which is present individually or in the form of a tape, mat, hose or cord, or in the form of a bundle of continuous fibres.

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<sup>42</sup>  
~~39~~. The method according to claim <sup>26</sup>~~28~~, wherein constituent (d) comprises a silanised filler.

<sup>43</sup>  
~~40~~. The method according to claim <sup>26</sup>~~28~~, wherein constituent (d) comprises hydroquinone, hydroquinone monomethyl ether, pyrocatechol, 2,6-di-tert.-butyl-4-methylphenol.

<sup>44</sup>  
~~41~~. The object produced by the method according to claim <sup>26</sup>~~28~~.

<sup>45</sup>  
~~42~~. A process for producing a tooth filling by sequential layered solidification of a composition at positions corresponding to the cross-section of the filling in the particular layer, the process comprising solidifying in each layer a composition comprising the following constituents:

- (a) 2-99 wt.% of at least one compound comprising a group selected from an acrylate group, a methacrylate group, a vinyl group, an epoxy group, an oxetane group, an acryl-epoxy oligomer group or a methacryl-epoxy oligomer group, or at least one resin composition comprising at least one polymerisable polysiloxane,
- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator, and
- (d) 0-85 wt.% of one or more modifiers selected from the group consisting of fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

<sup>46</sup>  
~~43~~. The process according to claim <sup>45</sup>~~42~~, further comprising the steps of:  
a) producing a computer model of the filling to be produced,  
b) dividing the computer model into layers, which correspond in each case to a cross-section of the filling, and

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c) layered curing of the composition at positions corresponding to the cross-section of the filling under the action of visible light.

<sup>47</sup>  
~~44~~. The process according to claim <sup>45</sup>~~42~~, wherein the composition is a paste-like material.

<sup>48</sup>  
~~45~~. The process according to claim <sup>46</sup>~~43~~, wherein the composition is a paste-like material.

<sup>49</sup>  
~~46~~. The process according to claim <sup>46</sup>~~42~~, wherein constituent (a) comprises an ormocer.

<sup>50</sup>  
~~47~~. The process according to claim <sup>46</sup>~~42~~, wherein constituent (a) is a resin composition comprising polymerisable polysiloxanes, which can be hardened photochemically or thermally, in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon, wherein 1 to 100 mole %, based on the monomeric compounds, are selected from  
(i) silanes of the general formula (I),



wherein the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl, or NR'<sub>2</sub>

where R' = hydrogen, alkyl or aryl,

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Y = a substituent, which comprises a substituted or unsubstituted 1,4,6-trioxyaspiro-[4,4]-nonane radical,

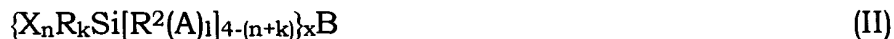
n=1, 2 or 3,

m=1, 2 or 3,

where  $n+m \leq 4$ ,

and/or from

(ii) silanes of the general formula (II),



wherein the radicals A, R, R<sup>2</sup> and X are the same or different, where all variables have the same meaning as defined above, and

A = O, S, PR', POR', NHC(O)O or NHC(O)NR',

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for  $l = 1$  and A = NHC(O)O or NHC(O)NR') or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R<sup>2</sup> = alkylene, arylene or alkylene-arylene,

k = 0, 1 or 2,

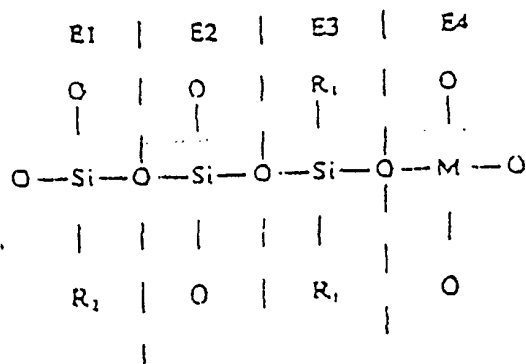
l = 0 or 1, and

x = a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B', when  $l = 1$  and A represents NHC(O) or NHC(O)NR'.

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48. The process according to claim 47, wherein the polymerisable polysiloxane further comprises a hydrolytically condensable compound of an element selected from the group consisting of B, Ba, Ti, Zr, Al, Sn, the

transition metals, the lanthanides and the actinides, or a pre-condensate derived from the above-mentioned compounds.

<sup>52</sup>  
49. The process according to claim <sup>46</sup>~~42~~, wherein constituent (a) is a resin composition comprising a compound composed of the structural element E 2 and at least one of the structural elements E 1, E 3 or E 4 of the general formula



wherein:

R<sub>1</sub> denotes a methyl, ethyl, n-propyl, isopropyl or an optionally CH<sub>3</sub>-C<sub>3</sub>H<sub>7</sub>-substituted phenyl radical,

R<sub>2</sub> denotes a CH<sub>2</sub>=CH, CH<sub>2</sub>=CHCOO(CH<sub>2</sub>)<sub>n</sub> or CH=C(CH<sub>3</sub>)-COO(CH<sub>2</sub>)<sub>n</sub> radical, or R<sub>1</sub>,

n denotes 0, 1, 2 or 3, and

M denotes titanium or zirconium.

<sup>53</sup>  
50. The process according to claim <sup>46</sup>~~42~~, wherein constituent (a) is present in a quantity of 10-95 wt. %.

<sup>54</sup>  
51. The process according to claim <sup>46</sup>~~42~~, further comprising hardening the composition using a wavelength range from 350-700 nm.

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52. The process according to claim 46, wherein constituent (a) comprises a component selected from the group consisting of aliphatic diurethane methacrylate, tetraethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates, 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate, 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 1,3,5,7,9-pentakis-3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexy-15,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane, bis-(3,4-epoxycyclohexylmethyl) adipate, monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl ether, triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether, ethylene glycol-monovinyl ether, diethylene glycol divinyl

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ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether and 2-diethylaminoethyl-vinyl ether.

56  
53. The process according to claim 42, wherein constituent (b) comprises

for free-radical hardening, a component selected from the group consisting of phosphine oxides, benzoin ethers, benzil ketals, acetophenones, benzophenones, thioxanthenes,  $\alpha$ -dicarbonyl compounds, bisimidazoles, metallocenes, aryl-tert.-butyl peresters and fluorones, or

for cationic hardening, a component selected from the group consisting of aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and phenylphosphonium-benzophenone salts, or a mixture thereof.

57  
54. The process according to claim 53, wherein constituent (b) comprises a component selected from the group consisting of diphenyl-2,4,6-trimethylbenzoylphosphine oxide, benzoin, benzoin-alkyl ether, benzildialkyl ketals,  $\alpha$ -hydroxyacetophenone, dialkoxyacetophenone,  $\alpha$ -aminoacetophenone, i-propylthioxanthone, camphor-quinone, titanocene, ferrocene, and 5,7-diiodo-3-butoxy-6-fluorone.

58  
55. The process according to claim 42, wherein constituent (c) comprises:

for free-radical hardening, a component is selected from the group consisting of tertiary amines, diaryl iodonium compounds, borates, organic phosphites and thioxanthenes,

for cationic hardening, a component is selected from the group consisting of xanthenes, fluorenes, fluorones and/or  $\alpha$ -dicarbonyl compound, or a mixture thereof.

<sup>59</sup>  
~~56~~. The process according to claim <sup>58</sup>~~55~~, wherein constituent (c) comprises a component is selected from the group consisting of N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine, and N,N-dialkyl-alkylaniline, butyrylcholine-triphenylbutyl borate.

<sup>60</sup>  
~~57~~. The process according to claim <sup>46</sup>~~42~~, wherein constituent (d) comprises an anthraquinone dyestuff.

<sup>61</sup>  
~~58~~. The process according to claim <sup>46</sup>~~42~~, wherein constituent (d) comprises a filler selected from the group consisting of silicon dioxide, pyrogenic silicon dioxide, amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glass, fragment polymer, silica gel, minerals, fibres and fabrics.

<sup>62</sup>  
~~59~~. The process according to claim <sup>61</sup>~~58~~, wherein constituent (d) comprises a fibre selected from the group consisting of glass fibres, carbon fibres, textile fibres and metal fibres, which is present individually or in the form of a tape, mat, hose or cord, or in the form of a bundle of continuous fibres.

<sup>63</sup>  
~~60~~. The process according to claim <sup>46</sup>~~42~~, wherein constituent (d) comprises a silanised filler.

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